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PHASE FORMATION IN CRYSTALLIZATION OF LITHIUM-ALUMINOSILICATE GLASSES WITH P_2O_5 ADDITIVE

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The effect of P_2O_5 additives on the regularity of changes in the phase composition of the crystallization products of the lithium-aluminosilicate system under different heat-treatment temperatures is investigated using the structural analysis methods. The conditions of emergence of β -quartz solid solutions as the only crystalline phase are identified.

The problem of producing glass ceramics based on the lithium-aluminosilicate system are widely discussed in the literature both in the development of glass ceramic compositions with an extremely low and negative TCLE, and in the synthesis of optically transparent glasses. The processes of phase transformations in this system without additional introduction of crystallization catalysts are well investigated [1–3], and there are numerous papers on the compositions and properties of lithium-aluminosilicate glasses with introduction of various catalysts and additives [3–7]. However, it should be noted that the majority of the developed glass ceramics belong to the low-lithium highly aluminous part of the system and are characterized by extremely high melting and molding temperatures ($> 1640^\circ\text{C}$), which restricts the possibilities of wide application of these glass ceramics for household purposes.

Of special interest are optically transparent glass ceramics based on this system [8] which have a TCLE value close to zero and can replace highly heat-resistant glasses, for example, quartz glass, and in doing so exhibit better technological properties. In developing such glass ceramics, it is recommended to add up to 5% ZnO and certain quantities of MgO, R_2O to the lithium-aluminosilicate system, and also $TiO + ZrO_2$ as crystallization catalysts [9–10]. However, apart from the specified additives, the introduction of P_2O_5 merits special attention, since it can play a double role as the crystallization catalyst and as the component reducing the melting temperature and improving the technological properties of the initial melt.

We investigated the effect of P_2O_5 on the phase formation processes in the heat treatment of glasses of the lithium-aluminosilicate system. The main ultimate purpose of the investigation was to obtain an optically transparent glass ceramic material with good technologic properties. However, it

is known that introduction of minor additives to a system can have a significant effect on the phase formation processes. It was taken into consideration that the most desirable crystalline phases in transparent glass ceramics is β -quartz solid solution.

The following region of the compositions was studied: (% , here and elsewhere molar content is indicated): 62–74 SiO_2 , 12–24 Al_2O_3 , 4–16 Li_2O (with a constant content of minor additives R_mO_n (10%); P_2O_5 was introduced instead of SiO_2 in the amount of 4 and 8%.

The mixtures were prepared of VC-1 quartz sand, chemically pure aluminum, titanium oxide (IV), lithium carbonate, zinc oxide, sodium carbonate, and zirconium dioxide.

The glasses were melted in a gas-flame furnace in corundum crucibles at the maximum temperature of 1550°C and held at this temperature for 3 h. All glasses were completely melted and clarified, except for the compositions with 24% Al_2O_3 content (the latter had a crust). The glasses were cast on a cooled metal plate. Since the TCLE of the glasses was relatively low (the estimated value of 50×10^{-7} – $60 \times 10^{-7} \text{ K}^{-1}$), the glasses were not annealed, in order to avoid the risk of generating crystallization centers in the course of annealing.

Figure 1 shows the results of melting glasses with different contents of P_2O_5 . As the content of P_2O_5 increases, the glass formation regions are slightly expanded toward an increased content of Al_2O_3 . The technological properties improve as well: the glasses become less viscous.

The differential thermal analysis of the considered glass sections indicated the presence of two exothermic effects: a weakly expressed low-temperature effect and an intense high-temperature effect (Fig. 2). According to the x-ray diffraction analysis data, the first effect is determined by the emergence of β -quartz solid solutions, and the second is determined by β -spodumene. With a significant content of

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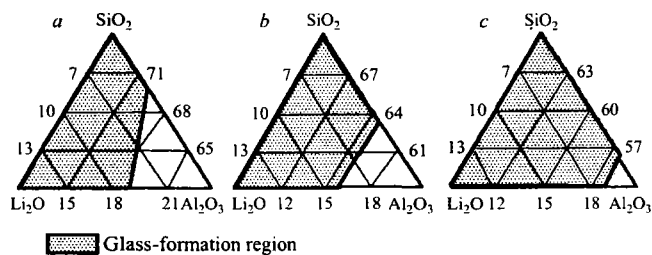


Fig. 1. Glass-forming capacity of glasses with a molar content of 10% $R_m O_n$. Molar content of P_2O_5 : a) 0%; b) 4%; c) 8%.

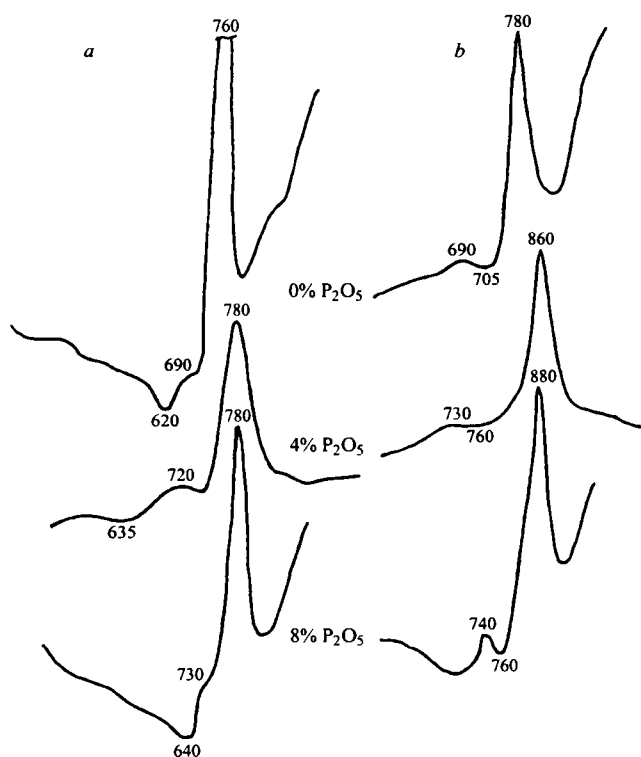


Fig. 2. Derivatogram of glasses with different molar contents of P_2O_5 : a) 16% Li_2O and 12% Al_2O_3 ; b) 10% Li_2O and 12% Al_2O_3 .

Li_2O (16%), the effect of P_2O_5 on the crystallization process is insignificant: the temperatures of both exothermic effects increase by 20–30°C and are brought somewhat nearer (the temperature interval between the exothermic effects is 70, 60, and 50°C). With the Li_2O content equal to 10%, the effect of P_2O_5 is more significant. The temperature of the second exothermic effect increases from 780 to 865–880°C, and the first exothermic effect becomes more perceptible. In this case, the temperature interval between the exothermic effects increases significantly up to 140°C.

Since it is desirable for the β -quartz solid solution to be the only crystalline phase in the synthesis of transparent glass ceramics, the increase in the interval between the temperatures of the formation of both phases is of great significance. An introduction of 4% P_2O_5 to the compositions with

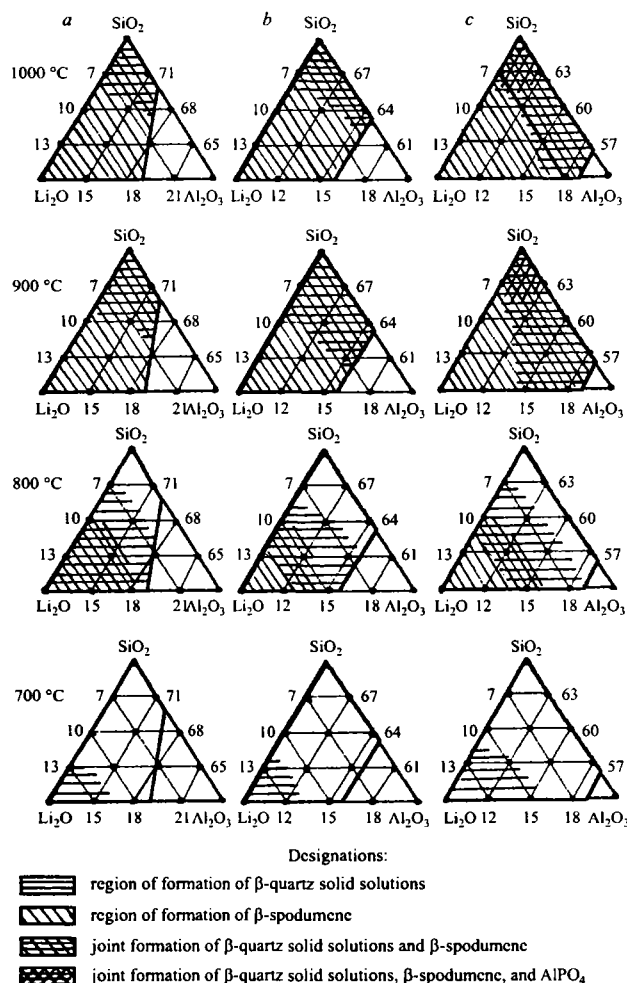


Fig. 3. Phase formation in glasses of lithium-aluminosilicate system with 10% content of $R_m O_n$. Molar content of P_2O_5 : a) 0%, b) 4%, c) 8%.

10% Li_2O leads to favorable conditions for low-temperature heat treatment without β -quartz solid solutions being transformed to spodumene. Therefore, further investigation was carried out on glasses that contained 4% P_2O_5 and 10% Li_2O .

The regularities of changes in the phase composition of the crystallization products depending on the composition of the synthesized glasses are of particular interest. With the optimum heat treatment regime, the β -quartz solid solutions can be produced as a unique crystalline phase, but with a further increase in the heat-treatment temperature, this phase changes over to β -spodumene solid solutions which abruptly decrease the optical transparency; the β -quartz solid solutions can be obtained in the form of crystals whose size is below the visible light wavelength ($< 0.4 \mu m$), and moreover, the refractive indexes of the residual vitreous phase and the crystals in these solutions differ insignificantly.

Figure 3 shows the regions of the crystalline phase formation for the heat treatment of the experimental glasses performed at 700, 800, 900, and 1000°C for 2 h. The heat treat-

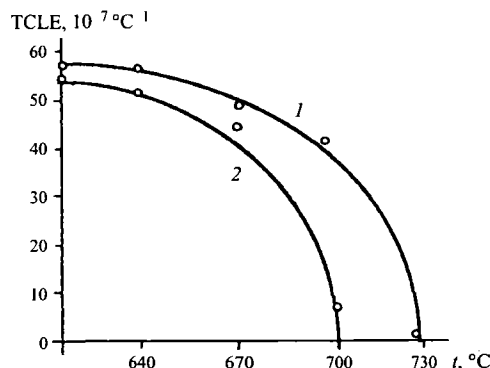


Fig. 4. The effect of the temperature of primary heat treatment of glasses containing 10% (1) and 16% (2) Li_2O on variations in the TCLE.

ment at 700°C produces the crystalline phase (β -quartz solid solutions) only in the glasses containing 13% and up Li_2O . With an increase in the content of P_2O_5 , the region of formation of β -quartz solid solutions expands to the regions with a lower content of Li_2O , i.e., 10%. All other glasses remain x-ray-amorphous. At 800°C, a substantial region of β -quartz solid solutions was identified, which were formed simultaneously with β -spodumene solid solutions, and the sections with 4 and 8% P_2O_5 exhibited β -spodumene solid solutions as the only crystalline phase. With increasing heat treatment temperature, the region of β -spodumene solid solutions expands, and the β -quartz solid solutions are only retained in the low-lithium compositions. The formation of a new phase, $AlPO_4$, was identified in the low-lithium region in the sections with 8% P_2O_5 at temperatures of 900 and 1000°C.

Thus, in high-lithium glasses, the formation of β -quartz solid solutions as the only crystalline phase can be expected only when the heat treatment temperatures do not exceed 700°C. It is precisely these compositions that retain their transparency in heat treatment.

The main diagnostic parameter in the conversion of glass to optically transmitting glass ceramics is the TCLE. To study the effect of the heat treatment of glasses on their TCLE, glass samples containing 4% P_2O_5 and 10% Li_2O were heat-treated for 1 h at temperatures of 640, 670, 700, and 750°C. The glasses retained their transparency at the specified temperatures. An abrupt decrease in the TCLE was registered in these glasses, as compared to the reference glasses without heat treatment (Fig. 4), which is evidence of

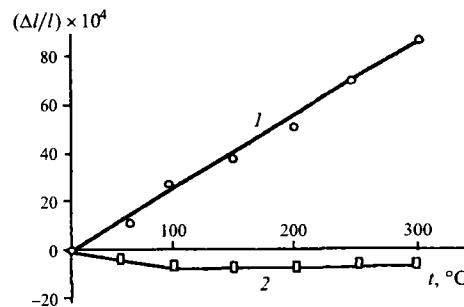


Fig. 5. Temperature dependence of relative elongation of glass containing 4% P_2O_5 and 10% Li_2O : 1) without heat treatment; 2) heat treatment at 750°C.

active processes of β -quartz solid solution crystallization in these glasses. The results of heat treatment are especially obvious in Fig. 5.

Thus, the favorable effect of P_2O_5 additives on the technological and crystallizing properties of lithium-aluminosilicate glass is validated.

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